The Study of Effect of Polymer on the Conductivity of the Solid Polymer Electrolytes

Dishun Zhao, Xinchen Zhang[1], Ying Li, Fengxia Sun, Junfang Zhao[2], Juwei Qin, Huanzhang Chen, Peiwen Xiong

Hebei University of Science and Technology

Department of Chemical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei, 050018, P. R. China

Since Wright and coworkers discovered that complex compound of polyethylene-oxide (PEO) and alkaline metal had ionic conductivity, the intensive research have been conducted in the field of solid polymer electrolytes.

A solid polymer electrolyte (SPE) with melting solid of urea and inorganic salts has been prepared in our lab. Doped small amount of polymer, the conductivity increased to 6.84×10^{-3} S/cm at room temperature [1]. The purpose of this research is to investigate the effect of polymers on the conductivity of SPE consisted of urea-salts melting solid.

1. The effect of inorganic salts on conductivity

Experimental results based on different inorganic salts, LiSCN, NaSCN, LiCl and $LiClO_4$ (Data were not shown here) illustrated that there was an optimum ratio between urea and inorganic salt, at which SPE gave a maximum conductivity. It had been found that salts had obvious effect on the conductivity of SPE. A relatively low lattice energy is beneficial to form melting solid system with high conductivity and low co-melting point. $LiClO_4$-urea with mole ratio of 1: 4.5, achieving a conductivity of 1.84 × 10 -3 S/cm, was the best one in the four salts used in our experiment.

2. The effect of polymer content on conductivity

Various polymers, PEG, PAN-NH_4, and PEGAc, were used in doping into $LiClO_4$-urea. The conductivity increased with the raise of polymer content in SPE at the beginning. Upon reaching the maximum value, conductivity began to decrease with more polymers added into SPE. After that, the system conductivity decreased with the polymer content up.

3. The effect of polymer structure on conductivity

Three polymers, PEG, PEGAc, and PAN-NH_4, were doped into $LiClO_4$-urea melting solid (mole ratio 1:4.5) separately. Table 2 summarized the conductivity of SPE at room temperature. It has been found that different polymers have distinct solubility in melting solid. For example, PVA becomes poorly compatible with melting solid when its content is higher than 0.7% (weight %), while the critical value of PEG can get to 30% in this case. The units of PEG and PEGAc, -CH_2CH_2O- and -$CH_2COOCH_2CH_2COO$-, have oxygen atoms, which have a high electronegrativity enduing a strong polarity to polymer chain. This characteristic makes them more compatible with melting solids than PAN-NH_4. From another point, the good compatibility between salts and urea can also improve conductivity.

4. The effect of heating temperature on conductivity

When the heating temperature was controlled under 140°C, the conductivity of SPE under room temperature was found to be higher than that of over 160°C.

5.The apparent activation energy of variety of SPE

From the relationship between SPE conductivity and temperature of PEG-$LiClO_4$-urea, PEGAc- $LiClO_4$-urea, and PAN-NH_4-$LiClO_4$-urea systems, it is concluded that the conductivity and temperature could match in the VTF equation derived from amorphous free volume theory.

The apparent activation energy, which indicates the difficulty of ion transition, were calculated and summarized in table 1. A small Ea indicates the ions' easy transition and thus high conductivity. System PEG-$LiClO_4$-urea had the lowest Ea and highest conductivity, which can be seen from table 1, while PAN-NH4-$LiClO_4$-urea system demonstrated a high Ea with low conductivity. These results match the theory perfectly and indicate the SPE system is noncrytal. With the optimum ratio of salts and urea, the system has a good compatibility and forms homogeneous SPE colloid electrolyte.

Table 1. Activation energy and conductivity at room temperature of SPE based on LiClO4-urea.

Polymer	PEG	PEGAc	PAN-NH4
Polymer wt%	1.6	1.6	0.5
Conductivity (10^{3} S/cm)	1.85	1.83	0.686
Activation energy (J/mol)	1445	3866	4552

Conclusion

1. $LiClO_4$-urea-PEG is an effective SPE system. Its conductivity at room temperature can reach 1.85 × 10 -3 S/cm under the optimum ratio of components.
2. The relationship between the conductivity of SPE made in experiment and temperature match the VTF equation derived from free volume theory.
3. The polymer with strong electronegativity groups is highly compatible with salt melting solid, thus generating high conductivity.

[1] *Shijiazhuang Normal School, Shijiazhuang, Hebei,050018 P.R. China*

[2] *Department of Chemistry, Beijing Institute of Technology, Beijing, 100080, P. R. China*